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# Shape- and size-selective photocatalytic reactions by layered titanic acid powder suspended in deaerated aqueous alcohol solutions

Bunsho Ohtani,\*\* Shigeru Ikeda,\* Hideaki Nakayama<sup>b</sup> and Sei-ichi Nishimoto<sup>b</sup>

- <sup>a</sup> Catalysis Research Center, Hokkaido University, Sapporo, 060-0811, Japan. E-mail: ohtani@cat.hokudai.ac.jp
- <sup>b</sup> Division of Energy and Hydrocarbon Chemistry, Kyoto University, Sakyo-ku, Kyoto 060-8501, Japan

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Protonic titanate of  $H_x Ti_{2-x/4} Z_{x/4} O_4 \cdot H_2 O$  (HLe;  $x \simeq 0.7$ , Z = vacancy) powder of a layered crystal structure was prepared, suspended in aqueous alcoholic solutions and photoirradiated by light of wavelength > 300 nm at room temperature under a deaerated atmosphere. HLe showed photocatalytic activity of  $H_2$  production, similar to ordinary titanium(IV) oxide powders. The rate and time course of  $H_2$  evolution by HLe depended strongly on the kind of alcohol. Detailed investigation revealed that the photocatalytic activity was regulated by the shape and size of the alcohol, due to the selection of adsorption at the interlayer of HLe.

# 1. Introduction

Photocatalytic reactions occurring on the surface of photoirradiated semiconductors have attracted much attention by scientists. Their possible environmental applications,<sup>1-3</sup> such as photoinduced removal of contaminated harmful chemicals in indoor and outdoor atmospheres, are now in the stage of practical testing by many companies, especially those in Japan.<sup>3</sup> Although, in such decomposition of organic materials, their chemical bonds are cleaved non-selectively mainly by positive holes that are formed in the valence band of the semiconducting materials as a result of photoexcitation of electrons into the conduction band, it has been clarified that under selected reaction conditions, e.g., in the absence of molecular oxygen, one can expect selective organic reactions.<sup>4-7</sup> For example, we have shown that an amino acid, lysine, undergoes selective deaminocyclization into piperidine-2-carboxylic acid (pipecolinic acid) by aqueous suspensions of titanium(IV) oxide  $(TiO_2)^8$  or cadmium(II) sulfide (CdS).<sup>9</sup> The use of platinized TiO<sub>2</sub> enabled us to synthesize optically active pipecolinic acid selectively and efficiently.9

In order to realize further useful applications of photocatalytic reactions to organic synthesis, the addition of selectivity for specific reactions or products is necessary. One possible strategy to give size and/or shape selectivity to the photocatalysts is the incorporation of a photocatalyst (e.g.,  $TiO_2$ ) into porous materials (e.g., zeolites)<sup>10-12</sup> and modification of the photocatalyst surface with organic compounds. However, there are the problems that the porous materials absorb or scatter the light for excitation of photocatalysts and that the surface-attached compounds undergo photocatalytic decomposition. One possible way to overcome these problems is to use a photocatalyst whose structure has an inner surface, *i.e.*, a photocatalyst with a layered, tunnel or porous crystal structure. We have reported the photocatalytic reaction of  $TiO_2$  crystallites with a tunnel structure,  $TiO_2(B)$ , but the size of the tunnel was too small (ca. 0.4-0.7 nm in inner diameter) to induce selective photocatalytic reaction,<sup>13</sup> though we could observe its photocatalytic activity.

As a crystal structural modification of titanic acid, TiO<sub>2</sub> ·  $nH_2O$ , lepidocrocite-like titanic acid,  $H_xTi_{2-x/4}Z_{x/4}O_4$  ·  $H_2O$  (HLe,  $x \simeq 0.7$ , Z = vacancy), has been synthesized.<sup>14–16</sup> Preliminary experiments by Domen's group have shown that the platinized HLe has sufficient photocatalytic activity when irradiated in methanol-water mixed solvent to liberate molecular hydrogen (H<sub>2</sub>) and that the rate of H<sub>2</sub> evolution from  $C_1-C_4$  straight-chain alcohols decreased along with the chain length.<sup>17</sup> Assuming that the photocatalytic reaction of these alcohols occurred at the inner surface between the TiO<sub>x</sub> layers of HLe, it can be expected that such a tendency for the reaction rate to depend on the size of the substrate can be used for selection of molecular size or shape by the entrance of the inner part of the photocatalyst. In this study, we examined the photocatalytic reaction of HLe with a wide range of substrates under various reaction conditions, and we obtained evidence of size- and shape-selective photocatalytic reaction by HLe.

## 2. Experimental

#### 2.1. Materials

HLe powder was synthesized according to the previously reported methods.<sup>14–16,18</sup> A brief summary of the procedure is as follows. A mixture of anatase  $TiO_2$  powder (Merck) and caesium carbonate ( $Cs_2CO_3$ , Wako Pure Chemical Industries) was heated at 1073 K for 40 h. The product,  $Cs_xTi_{2-x/4}Z_{x/4}O_4$  (CsLe; Z = vacancy), was suspended in *ca.* 1 mol dm<sup>-3</sup> hydrochloric acid for 72 h to give HLe. Degussa P-25 TiO<sub>2</sub>, which does not have a porous structure, was used as a representative photocatalyst. Platinization (0.5 wt.%) of P-25 TiO<sub>2</sub> was achieved by impregnation followed by H<sub>2</sub> reduction, as reported previously.<sup>19</sup> Methanol, ethanol, propan-2-ol, propan-1-ol, butan-1-ol, butan-2-ol and *tert*-butyl alcohol, all of the highest available grades, were purchased from Wako (with the exception of *tert*-butyl alcohol; Nakalai Tesque) and used without further purification. Hydrated hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub> · xH<sub>2</sub>O) was supplied from Nakalai.

#### 2.2. X-ray diffraction analysis

A Rigaku Geigerflex 2013 diffractometer (CuK $\alpha$ , Ni filter, 35 kV, 20 mA) was used to record diffractograms at a scanning rate of 1 deg min<sup>-1</sup> (ref. 19).

#### 2.3. Transmission electron microscopy

A Hitachi H-800 electron microscope operated at 200 kV acceleration voltage was used. The procedure for preparing a TEM sample on microgrids has been reported previously.<sup>8</sup> Electron diffraction patterns were recorded in the apparatus with a camera length of 0.75 m.

#### 2.4. Photocatalytic reaction

A 50 mg portion of photocatalyst power, HLe or  $\text{TiO}_2$ , was suspended in a mixture of alcohol and water (in most cases 50/50 vol.% except for butan-1-ol and butan-2-ol, see text) and deaerated by bubbling of argon (Ar) for at least 15 min. To avoid volatilization of alcohols during the bubbling, the suspensions were chilled in an ice bath. The deaerated suspension in a sealed glass tube that transmits light of wavelength > 300 nm was irradiated by a 400 W mercury arc (Eiko-sha) at 298 K under magnetic stirring (1000 rpm).

## 2.5. Product analyses

Products in the gas phase, molecular hydrogen (H<sub>2</sub>), were analyzed using a Shimadzu GC-8A gas chromatograph (GC) equipped with a molecular sieve 5A column and a thermal conductivity detector (TCD). A portion of the gas phase of the reaction vessel was withdrawn with an airtight syringe and injected into the GC during and after the photoirradiation. For the product from aqueous propan-2-ol solution, a sample obtained after centrifugation to remove the photocatalysts was analyzed using a Shimadzu GC-7A gas chromatograph equipped with a PEG20M column and a flame ionization detector (FID).

# 3. Results and discussion

#### 3.1. Preparation of HLe

X-ray diffraction (XRD) patterns of CsLe and HLe were in good agreement with those reported previously.<sup>14–16</sup> The molar ratio of vacancies, x, was not determined in this work, but, based on the coincidence of XRD patterns we assumed

that the ratio was *ca*. 0.7 as reported previously.<sup>14–16</sup> Fig. 1(a) shows a TEM picture of HLe.

Flat plates of size ranging from a few tens of nanometres to a few micrometres were seen in all of the views. Detailed inspection revealed that there were many steps, as indicated by different degrees of darkness of the image, at which the density of electrons in the sample changed. This fact confirms that HLe had a layered structure. Evidence of the HLe structure was also obtained from electron diffraction patterns of the sample powders. A representative pattern is shown in Fig. 1(b). An expected reciprocal lattice drawn by assuming that the HLe crystallite has its (010) plane perpendicular to the electron beam is also shown in Fig. 1(c), and it is obvious that the apparent electron diffraction pattern is reasonably interpreted by the layered structure of HLe. The results of TEM observation of platinized HLe are discussed in a later section.

# 3.2. Photocatalytic reaction of HLe with methanol and propan-2-ol

HLe was suspended in 50 vol.% aqueous solution of methanol or propan-2-ol and irradiated at 298 K under an Ar atmosphere. A small portion of hexachloroplatinic acid, containing Pt atoms corresponding to 0.5 wt.% for HLe, was added to be reduced *in situ* to platinum metal deposits. The time course of the reaction is shown in Fig. 2(a).

Just after commencement of photoirradiation, liberation of  $H_2$  in the methanol system could be seen and its rate was almost constant during the 9 h period of irradiation, while an appreciable induction period, *ca.* 3 h, was observed for the propan-2-ol system and the rate of  $H_2$  liberation after the induction period was much smaller, *ca.* 1/10, than that in the methanol system. In both systems,  $H_2$  evolution could be seen only under the condition of photoirradiation, indicating that this reaction is "photocatalytic". In the control experiment in which hexachloroplatinic acid was not added, the bare HLe gave a negligible amount of  $H_2$ . Consequently, *in situ* deposited Pt enhances the  $H_2$  evolution, as commonly seen for TiO<sub>2</sub> photocatalytic reactions.<sup>8,20–22</sup> On the basis of these results, one possible interpretation of the induction period in the propan-2-ol system is that the period corresponds to the time



**Fig. 1** (a) A TEM picture of HLe. (b) An electron diffraction pattern of an HLe particle. (c) An expected reciprocal lattice obtained on the basis of the assumption that the HLe crystallite has its (010) plane perpendicular to the electron beam in TEM. (d, e) TEM pictures of HLe with (d) *in situ* photodeposited and (e) impregnated Pt particles.



Fig. 2 (a) Time courses of photocatalytic  $H_2$  production from aqueous (50 vol.%) methanol (open circles) and propan-2-ol (closed circles) in the presence of suspended HLe particles. Hexachloroplatinic acid solution containing 0.5 wt.% Pt was added before irradiation to be deposited during the photoirradiation. (b) Platinized HLe powders were recovered from the experiment in part (a), dried and used again in this experiment. Symbols are the same as those in (a).

for the complete reduction of hexachloroplatinic acid by the following reaction:

$$H_2PtCl_6 + 2R^1R^2CHOH = Pt + 2R^1R^2CO + 6HCl$$
 (1)

 $(R^1 = R^2 = H$  for methanol and  $R^1 = R^2 = CH_3$  for propan-2-ol) along with the dehydrogenation of alcohols to liberate  $H_2$  (refs. 20, 22):

$$R^{1}R^{2}CHOH = R^{1}R^{2}CO + H_{2}$$
(2)

In this study, we detected almost the stoichiometric amount of acetone in the propan-2-ol system, but we did not try to analyze formaldehyde. Previous experiments using  $TiO_2$  as a photocatalyst have shown the stoichiometric, *i.e.*, 1 : 1, formation of formaldehyde with H<sub>2</sub> from methanol.<sup>20</sup>

Fig. 1(d) shows a TEM picture of a Pt-deposited HLe photocatalyst. Small Pt deposits of a few nanometres in size were observed. Careful inspection of the TEM picture showed that most of these Pt deposits were located along the step lines, *i.e.*, at the edge of the sheet or layer, rather than on the flat terrace. It is presumed that such deposition proceeds via two steps: reduction of hexachloroplatinic acid into Pt atoms by photoexcited electrons in HLe, and coagulation of the atoms into Pt deposits of nanometre size. However, in a photocatalytic reaction, the deposited Pt can be a site for the reduction. Therefore, we presumed that the reduction of hexachloroplatinic acid proceeds at the step edge rather than on the terrace. Previous reports have suggested that the interlayer of HLe crystallite acts as a cation exchange material<sup>16</sup> and, thereby, hexachloroplatinic acid, an anion, may not be incorporated into HLe. This is another reason for the Pt deposition at the step edge. Platinization of HLe was also performed by impregnation-H<sub>2</sub> reduction. As also shown in Fig. 1(e), this procedure tended to produce aggregates of Pt particles, and lower photocatalytic activity (ca. 3  $\mu$ mol h<sup>-1</sup>) was observed, presumably due to insufficient Pt loading; only a part of HLe platinized. Therefore, in situ photodeposition was was



**Fig. 3** Photocatalytic activity of *in situ* platinized HLe suspended in aqueous (50 vol.%) methanol solution as a function of the amount of Pt loading.

employed for platinization of HLe throughout this study. Fig. 3 shows the dependence of photocatalytic activity in the aqueous methanol solution on the amount of Pt loaded by photodeposition.

The H<sub>2</sub> evolution was negligible without Pt loading, and the rate increased with Pt loading up to 0.2–0.5%. Further loading at >1 wt.% reduced the activity, maybe due to the enhancement of electron–positive hole recombination. Similar behavior has been observed for an ordinary TiO<sub>2</sub> photocatalyst.<sup>8</sup> In the subsequent experiments, HLe platinized at 0.5 wt.% *in situ* was used.

If we assume that the rate of reaction (1) is much slower when propan-2-ol is employed, *i.e.*, the oxidation of propan-2ol by positive holes as a counter-reaction to Pt deposition is slower than that of methanol, the presence of an induction period as shown in Fig. 2(a) can be rationalized. However, the following results made us consider another reason. Fig. 2(b) shows the time course of photocatalytic  $H_2$  evolution from methanol and propan-2-ol solutions, in the absence of hexachloroplatinic acid, with a suspension of HLe that was preloaded with Pt before the commencement of photoirradiation. A powder of HLe recovered from each photoirradiated (9 h) suspension and dried was used in these experiments. The methanol system showed almost the same time course as that in Fig. 2(a), suggesting that the time for Pt deposition is short enough in this case. On the other hand, the induction period for the propan-2-ol system was shortened by the use of a Ptpreloaded HLe photocatalyst. These results suggest that the induction period seen in Fig. 2(a) was due mainly to the time needed for the in situ Pt deposition, but another reason still existed to give an appreciable induction period in Fig. 2(b).

Fig. 4 shows the time courses of H<sub>2</sub> evolution from methanol and propan-2-ol solutions with three kinds of Pt-loaded HLe powders: Pt photodeposited from methanol by 4 h irradiation (M-4) and from propan-2-ol by 2 h irradiation (during the induction period) and by 14 h irradiation (at constant photocatalytic activity). Again, the methanol system showed almost the same time-course curves regardless of the kind of photocatalyst, and the propan-2-ol system gave curves that were slightly different from each other. It is obvious that the rates of H<sub>2</sub> evolution, when they are compared at the time after the induction period, were not so different if the same alcohol was used; the rate was predominantly controlled by the kind of alcohol used, but not by the kind of photocatalyst. The data in this figure also indicate that the in situ Pt deposition might have been completed in the propan-2-ol system even during the induction period, since the P-2 catalyst showed comparable or even higher photocatalytic activity in both systems. This also suggests that at least a part of the induction period was due to a factor other than the time for



**Fig. 4** Time courses of photocatalytic  $H_2$  production from aqueous (50 vol.%) methanol (open symbols) and propan-2-ol (closed symbols) in the presence of HLe particles with *ex situ* deposited Pt. Circles: HLe recovered from 4 h irradiated suspension of methanol. Triangles: HLe recovered from 2 h irradiated suspension of propan-2-ol. Squares: HLe recovered from 14 h irradiated suspension of propan-2-ol. Photodeposition of Pt was carried out under the same conditions as in Fig. 2.

Pt deposition, *e.g.*, time for incorporation of alcohol molecules into the interlayer spaces in the HLe photocatalyst.

Fig. 5 shows the influence of time of contact before the commencement of photoirradiation. The following three samples were prepared. (a) HLe powder was suspended in an aqueous solution of alcohol and kept in the dark under an Ar atmosphere for 42 h, and a solution of hexachloroplatinic acid was added just before irradiation. (b) HLe powder was suspended in an aqueous solution of hexachloroplatinic acid and kept in the dark under an Ar atmosphere for 42 h. Alcohol



**Fig. 5** (a) Time courses of photocatalytic  $H_2$  production from aqueous (50 vol.%) methanol (open symbols) and propan-2-ol (closed symbols) in the presence of HLe particles. Circles: HLe and aqueous alcoholic solution were mixed for 42 h before irradiation. Triangles: HLe and hexachloroplatinic acid solution were mixed for 42 h before the irradiation. Squares: HLe, alcohol, and hexachloroplatinic acid solution were mixed just before photoirradiation. (b) HLe powders were recovered from the reaction mixture of the experiment in part (a) and used. Symbols are the same as those in (a).

was added, and the suspension was purged of air by Ar bubbling for 15 min before irradiation. (c) HLe powder, an aqueous solution of alcohol and hexachloroplatinic acid were mixed, and the resulting suspension was purged of air for 15 min before irradiation (standard procedure).

The methanol system was also insensitive to these reaction conditions and gave almost the same time-course curves in all cases. On the other hand, the time of contact had an influence on the photocatalytic reaction of propan-2-ol; contact of the HLe photocatalyst with propan-2-ol for a long time shortened the induction period a little, but the steady state rate of  $H_2$ evolution was not greatly affected, as was seen after ca. 6 h irradiation. These findings suggest that the photocatalytic reaction of propan-2-ol proceeds at the interlayer of the HLe photocatalyst and that a considerably long contact time is necessary to obtain a steady-state reaction rate. To exclude the induction time due to the Pt photodeposition, the Ptloaded HLe powders were recovered, washed with water, dried, and re-used in the photocatalytic reactions. Fig. 5(b) shows the results. As expected, the methanol system did not show any marked difference and the long-time contact was necessary for the photocatalytic H<sub>2</sub> production from propan-2-ol, though the induction period was greatly shortened by pre-deposition of Pt.

At present, we have no direct experimental evidence of the reaction mechanism, including the incorporation of alcohol molecules into the interlayer of the HLe photocatalyst. However, if we assume that methanol molecules, which are smaller than propan-2-ol molecules, can easily access the interlayer but that propan-2-ol molecules cannot, the sensitivity of the reaction rate toward the reaction conditions must be more marked in the propan-2-ol system than in the methanol system, as described above.

#### 3.3. Photocatalytic H<sub>2</sub> evolution from various alcohols

Several aliphatic alcohols were used as substrates for the photocatalytic reaction of HLe. Fig. 6 shows the steady-state rates of  $H_2$  evolution by HLe with *in situ* and *ex situ* deposited Pt. Except for methanol and ethanol, the time courses of  $H_2$  evolution from these alcohols showed an induction period



**Fig. 6** Steady-state rate of photocatalytic  $H_2$  production from aqueous alcohol solutions by *in situ* (left, full bars) and *ex situ* (right, open bars) platinized (0.5 wt.%) HLe particles (a) and *ex situ* platinized (0.5 wt.%) P-25 particles (b). The concentration of alcohol was 50 vol.%, except for butan-1-ol (5.8 vol.%) and butan-2-ol (6.7 vol.%).

 Table 1
 Photocatalytic H<sub>2</sub> production from aqueous alcohol solutions by in situ (0.5 wt.%) platinized HLe particles

Alcohol	Abbrev.	Concentration (%)	$H_2$ production <sup><i>a</i></sup> /µmol h <sup>-1</sup>	Induction period /h
Methanol	MeOH	50	11.0	~0
Ethanol	EtOH	50	7.2	~0
Propan-1-ol	Pr-1-OH	50	1.4	1.0
Propan-2-ol	Pr-2-OH	50	1.2	1.5
Butan-1-ol	Bu-1-OH	5.8	0.2	2.8
Butan-2-ol	Bu-2-OH	6.7	0.5	4.0
tert-Butyl alcohol	t-BuOH	50	0.6	3.5

<sup>*a*</sup> Quantum efficiency of  $H_2$  evolution from methanol solution was calculated to be *ca*. 0.4% from the results of previous experiments<sup>23</sup> using the same photoirradiation setup for TiO<sub>2</sub>.

(as observed and shown in the previous section for the propan-2-ol system), the period of which was increased with the order shown in Table 1.

The smaller activity of HLe with pre-deposited Pt compared with the *in situ* platinized one was commonly seen for these alcohols; however, both platinized HLe powders showed similar tendencies in the rate depending on the kind of alcohol. The order obeyed the general rules of: (1) a higher rate with a small number of carbon atoms, and (2) a higher rate of straight chains than branched alkyl groups among isomers of the same molecular weight. The exceptions of butan-1-ol and butan-2-ol may be due to their lower concentrations in the reaction mixture. In these experiments, H<sub>2</sub> evolution is attributable to the reaction (2) (intramolecular dehydrogenation), except for *tert*-butyl alcohol, which undergoes intermolecular dehydrogenation and oxidative scission to give acetone.<sup>21</sup>

Similar photocatalytic reactions were carried out by using platinized P-25  $\text{TiO}_2$ , which is known to consist of nonporous spherical primary particles without size-selective pores or spaces. As shown in Fig. 6(b), the activity was more than one order of magnitude higher than that of HLe. Notably, ethanol, but not methanol, gave the maximum rate in the case of P-25 TiO<sub>2</sub>, and reduction in the rate due to the alkyl chain length and branching was not so obvious. (Relatively lower activities for butan-1-ol and butan-2-ol were also observed.)

These different behaviors of HLe and the non-porous P-25 support the hypothesis of a photocatalytic reaction mechanism of HLe, including penetration of the substrate alcohol into the inner space between the layers and oxidation by photogenerated positive holes. This is also supported by the fact that P-25  $TiO_2$  gave negligible induction period for all the kinds of alcohol used in this study. The shapes and sizes of the alcohols to be adsorbed in the HLe controlled the rate of photocatalytic reaction. Thus, a mechanism of shape- and size-selective photocatalytic reaction has been proved as follows. The HLe catalyst consisted of TiO, layers, as was directly observed by TEM, and in situ photodeposition of Pt occurred at the step edge of layers, since an anionic  $PtCl_6^{2-}$ cannot be adsorbed in the interlayer of anionic  $TiO_x$ . The substrate alcohol penetrates into HLe by exchange of asincorporated water molecule. The rate and saturated amount of adsorption of each alcohol in HLe, though they were not directly measured, depended on the size and shape of each alcohol.

# 4. Conclusion

It has been proved that HLe, having a layered crystal structure, shows sufficient photocatalytic activity for  $H_2$  production, along with oxidation of alcohol, from aqueous alcoholic solutions. The  $H_2$  production rate depended strongly on the size and shape of the alcohol, unlike the dependence of the non-porous  $\text{TiO}_2$  photocatalyst, suggesting that size and shape selection are achieved in HLe. This is the first reported example of a selective photocatalytic reaction, except for the preliminary results by Domen's group.<sup>17</sup> Investigation of extensions of the reaction substrate, *e.g.*, amines or carboxylic acids, is now under way.

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